CdTe AND CdTe : Hg ALLOYS CRYSTAL GROWTH USING STOICHIOMETRIC AND OFF-STOICHIOMETRIC ZONE PASSING TECHNIQUES

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Résumé. — En vue de la croissance de cristaux de CdTe de haute résistivité, on étudie l'état thermodynamique de matériaux préparés par différentes méthodes de fusion de zone (fusion de zone en tube scellé, croissance en solvant tellure). De plus, on décrit une méthode, appelée *Sublimation THM*, qui permet de diminuer notablement les inconvénients liés à la croissance en solvant tellure (THM). Par ailleurs, afin d'augmenter le numéro atomique moyen des cristaux, on a réalisé des cristaux semi-isolants $\text{Cd}_{0,9}\text{Hg}_{0,1}\text{Te}$.

Abstract. — Some aspects of the thermodynamic state of CdTe crystals grown by different zone passing techniques (sealed ingot zone refining technique and THM in tellurium solvent) are considered with regard to the general objective of getting high resistivity crystals. A vapour growth technique, called *sublimation THM*, which reduces several drawbacks of classical THM using a tellurium solvent, is developed. The growth of semi-insulating $\text{Cd}_{0,9}\text{Hg}_{0,1}\text{Te}$ crystals, with the aim of increasing the average atomic number of the material, is presented.

1. Introduction. — Several of the main applications of cadmium telluride, as γ -ray detectors or laser windows, require a material with a low free carrier density and hence a high resistivity. For nuclear detection, a high atomic weight is also desirable. CdTe is a good candidate because its average atomic number is greater than that of germanium and could be increased by suitable alloying.

In the first part of the paper, we will consider some aspects of the thermodynamic state of CdTe crystals obtained by different zone passing techniques with regard to the general objective of getting high resistivity crystals.

The method of obtaining high resistivity crystals by stoichiometric vertical zone melting [1, 2] is not very reproducible and the material resulting from this technique is generally n-type and almost stoichiometric.

High resistivity crystals can also be obtained by THM growth using Te solution, either by doping with halogens [3] or without intentional doping [4]. These techniques present two important drawbacks: the irremediable presence of tellurium microprecipitates and a large concentration of traps resulting from growth conditions with a large departure from stoichiometry. A vapour growth technique, which could be called *sublimation THM*, reduces these drawbacks while keeping most of the advantages of classical THM using a tellurium solvent. Some preliminary results are presented.

In the second part, the growth of cadmium rich $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys by THM is presented. The composition $x = 0.9$ corresponds to an increase of the average

atomic number of CdTe which could theoretically lead to an increase of about 15 % of the photoelectric cross-section of the nuclear detectors.

2. Crystal growth of high resistivity CdTe by different zone passing techniques. — **2.1 VERTICAL ZONE MELTING OF STOICHIOMETRIC MELTS.** — It has been found possible to get high resistivity crystals by the sealed ingot zone refining technique for stoichiometric melts either by adjusting the melted zone temperature [1], or the thermodynamic conditions of the synthesis and growth of the material before zone refining [2].

These methods are not reproducible because other factors are crucial to achieve an exact compensation, such as the nature and concentration of residual impurities. The crystals obtained after vertical zone refining are generally n-type with abnormally high mobilities at low temperature, sometimes a factor two higher than expected from the ionized impurities concentration [5], which cannot be explained in terms of zone purification efficiency. These anomalous high mobilities depend probably on two factors, firstly the deviations from stoichiometry, which are reduced by the particular equilibrium reached during zone melting. Secondly one can imagine that impurities assemble, during growth, or interact, to form highly compensated micro inhomogeneities or what Woodbury calls *distant defect pairing* [5], theoretically analyzed by Caillot [6]. This is assumed to depend on the annealing conditions the ingot sees just following growth. We have tried to modify these annealing conditions by adjusting the

temperature gradient which exists at the solid-liquid crystallization interface. This can be achieved by modifying the diameter of the zone melted ingots and consequently the heat flux.

For example, the thermal gradient in a gallium column enclosed in a silica tube and placed in a furnace having a gradient of 150 °C/cm in air, has been found equal to 50 °C/cm for a diameter of the Ga column of 16 mm and only to 30 °C/cm for a diameter of 20 mm [7].

We measure currently low temperature electron mobilities higher than $10^5 \text{ cm}^2/\text{V.s}$ on ingots grown in 15 mm I. D. tubes while we have not found mobilities higher than $6 \times 10^4 \text{ cm}^2/\text{V.s}$ on ingots grown in 20 mm I. D. tubes. The distant defect pairing is thus weaker in the case of a smaller thermal gradient : this confirms the relation between the distant defect pairing and the *quenching conditions* that the ingots undergo just following growth.

2.2 TRAVELLING HEATER METHOD USING A TELLURIUM SOLVENT. — It has been shown that high resistivity crystals can be obtained by THM using a Te solvent either by doping with halogens [3] (semi-insulating crystals) or without intentional doping [4] (crystals of resistivity 10^5 - $10^6 \text{ } \Omega \cdot \text{cm}$), the compensation of native defects being then achieved by the residual impurities. Stuck *et al.* [8] have recently developed a theoretical model of defects indicating that, in principle, semi-insulating CdTe can be grown directly without doping. The room temperature resistivity of intrinsic CdTe would be about $10^8 \text{ } \Omega \cdot \text{cm}$.

The condition to get this value is obviously the purity of the starting source material, which is for us a vertical zone refined ingot. If the purity of this source ingot is not sufficient, the result of THM is a low resistivity p-type material. It is then possible to perform a multi-pass THM, that is to use the purification effect of THM. The general trend is a simultaneous increase of resistivity and hole mobility, as can be seen on the following table (room temperature measurements).

TABLE I

Number of passes	$\rho \text{ } \Omega \cdot \text{cm}$	$\mu \text{ cm}^2/\text{V.s}$
1	380	33
3	1 800	87
4	$\simeq 10^5$	

The Travelling Heater Method using a Te solvent unfortunately presents two important intrinsic drawbacks owing to the composition of the grown crystal lying on the tellurium boundary of the homogeneity range of CdTe : firstly the inevitable presence of tellurium precipitates, due to the retrograde shape of the solidus line and to the growth in tellurium rich conditions, and secondly the necessity to compensate the large concentration of intrinsic defects (cadmium

vacancies) possible at the growth temperature, which give rise to a great number of traps.

Tellurium precipitates of 1 or 2 μ are clearly visible even under an infrared microscope.

An excess of tellurium atoms of 10^{17} cm^{-3} , corresponding roughly to the stoichiometric departure at 800 °C, can induce the presence of 2 500 precipitates, of diameter 1 μ , per mm^3 .

The presence of a so high amount of precipitates induces inhomogeneities which restrict the workable volume of crystals in nuclear detection and increase the residual infra-red absorption coefficient of laser windows.

We have tried to decrease the number of precipitates by postannealing. This has been achieved by moving up a hot zone along a CdTe ingot, (previously grown by THM), exactly like in the THM process, but without a solvent, i. e. in the solid state. The displacement speed of this zone corresponded to the classical growth rates in THM : $\simeq 6 \text{ mm per day}$. Moving up a zone at 900 °C along an ingot grown at 700 °C unfortunately modifies the electrical characteristics of the material which becomes conducting. A hot zone at 700 °C passing along an ingot grown at 900 °C does not modify the electrical conducting characteristics of the material nor does it not affect the state of the precipitates which remain visible and numerous.

2.3 SUBLIMATION TRAVELLING HEATER METHOD. — *Introduction.* — To reduce all the previously mentioned drawbacks of classical THM using tellurium, we have been led to develop a vapour growth technique using a similar arrangement [9].

The growth of cadmium telluride crystals from the vapour phase, by transport of a polycrystalline charge in closed or open tubes and recrystallization in a zone at lower temperature, has been widely reported by many authors [10, 11, 12, 13, 14, 15, 16, 17]. The crystals are generally of small size except those grown by Akutagawa and Zanio [16] who obtained untwinned single crystals up to volumes of 3 cm^3 .

Our method could be called *sublimation travelling heater method*. In this technique the tellurium-rich molten zone is replaced by an empty space having approximately the same dimensions (Fig. 1). A closed graphitized ampoule of internal diameter 15 mm contains a cadmium telluride source ingot and at its lower end an empty space of height 10 to 15 mm. By the slow movement of the charge relative to the heater, this empty space is made to migrate through the solid source material. The displacement leads to a temperature difference between the sublimation interface and the growth interface which induces a material flux from one to the other. A matching condition has to exist between the sublimation rate, which depends on the sublimation interface temperature, and the growth rate, which depends on the thermal gradient between the two interfaces and on the imposed lowering speed of the tube. Any disagreement between these para-

FIG. 1. — Principle of sublimation THM.

meters brings about a bad crystallization or even a dendritic structure.

It is possible to decrease the sublimation temperature and to increase the growth rate by the use of a chemical transport agent which can be for instance hydrogen or a mixture $\text{HCl} + \text{H}_2$. Then the chlorine simultaneously acts as transport and doping agent.

Compared to the classical vapour transport methods, the technical arrangement, furnace and tube, in the sublimation THM is very simple, and the length of the grown ingot only depends on the length of the source ingot, and not on the position and size of a particular temperature zone. The monitoring system can be rather rudimentary because vibrations have not a marked effect on this type of crystallization process. This sublimation THM possesses most of the advantages of classical THM using tellurium solvent :

- 1) Low growth temperature (in the 800-1 000 °C range) which minimized impurity pick up from silica tubes.
- 2) Low dislocation density and great crystalline perfection due to the low growth temperature and rate.
- 3) Purification with respect to the non volatile impurities which diffuse along the source ingot and concentrate in the remaining non sublimated part.

On the other hand, the total pressure $P(P_{\text{Cd}} + P_{\text{Te}_2})$ over solid CdTe tends, for thermodynamic reasons, to reach a minimum. This provides the condition

$P_{\text{Cd}} = 2 P_{\text{Te}_2}$ [18] and consequently the vapour tends to become stoichiometric. The composition of the grown crystals lies, in the three phase line diagram, near the P_{min} line, for which $P_{\text{Cd}} = 2 P_{\text{Te}_2}$, which is situated inside the homogeneity range and not very far from the line of *intrinsic* pure CdTe (Fig. 2). Conse-

FIG. 2. — Dependence of CdTe melting point on Cd pressure.

quently the grown crystals should not have a large tellurium or cadmium excess, that is no precipitates, and only a weak concentration of foreign impurities is involved in the compensation mechanism.

Results. — We have grown crystals at three temperatures, 800, 900 and 1 000 °C. The height of the empty space was around 12 mm : under these conditions, a very small temperature difference exists between the sublimation and growth interfaces. The imposed growth rate was in the range 5-7 mm per day. We used ingots purified by the sealed ingot zone refining technique as source material. Figure 3 presents an

FIG. 3. — Ingot grown at 900 °C by sublimation THM.

ingot grown at 900 °C at a speed of 6 mm per day. Growth figures, as triangles or sometimes squares, are visible on some crystallization interface facets which correspond to (111), (100) or (110) planes (Fig. 4).

FIG. 4. — Facets and growth figures on the crystallization interface.

The crystalline perfection of this material is attested by the quality of the Laue diagram pictured on figure 5 for a (110) facet. The ovalization of the spots comes from a mechanical focussing effect. We have not seen

FIG. 5. — Laue diagram of a (110) facet.

any precipitate by infrared microscopy in these crystals. A few dislocations only and no precipitates (perhaps some precipitates of very small size) are seen by electron scanning microscopy ⁽¹⁾ on crystals grown with a good adjustment of the growth parameters (900 °C-6 mm/24 h).

Two or three crystals are revealed on cross sectioning the ingot : better results could be probably obtained with a better adjustment of the different parameters.

We have not found any obvious relationship between the resistivity of the grown crystals and the growth temperature. Since the composition corresponds to a point lying inside the homogeneity range, this result is not surprising. A very small amount of residual impu-

⁽¹⁾ Observations carried out in Laboratoire d'Electronique et de Physique Appliquée by C. Schiller that we want to thank here.

rities can modify the electronic situation. Table II gives some room temperature electrical characteristics of the crystals.

TABLE II

Growth temperature °C	Net acceptor concentration cm ⁻³	Resistivity Ω.cm	Hall mobility cm ² /V. s
800	2.9×10^{15}	27	80
900	4.7×10^{15}	19	≈ 70
1 000	9.2×10^{14}	68	≈ 100

The crystals have been also characterized by photoluminescence measurements. Figure 6 shows the spectrum of an undoped crystal, registered at 4.2 K, which presents essentially a sharp excitonic line,

FIG. 6. — Luminescence spectrum of a crystal grown by sublimation THM at liquid helium temperature.

at 1.591 eV (attributed to the radiative annihilation of excitons trapped on neutral acceptors at $E_A = E_v + 0.05$ eV [19]) with two L. O. phonon replicas at 1.570 eV and 1.549 eV. No emission is seen in the 1.550 eV band edge region generally rich in impurity transitions [20]. Only a weak line at 1.473 eV emerges at lower energy, corresponding to the no phonon line of the so-called 142 eV band associated to

an acceptor complex at $E_v + 0.15$ eV, made up of a cadmium vacancy and a donor impurity [21] which could be residual aluminium atoms [22]. The different characteristics of this spectrum — only a predominant very sharp excitonic line, and a very weak emission associated to residual impurities — are typical of a very pure uncompensated sample.

The evaporation process has been highly accelerated, at 800 °C, by the presence of residual hydrogen which acts as a transport agent, while a neutral gas, such as nitrogen, does not affect the kinetics. Two ways have been followed to get semi-insulating crystals : the first was by using a previously chlorine doped ingot as source material ; the second, which is the most original, was by using a chlorine-hydrogen mixture as transport and doping agent.

3. Crystal growth of CdTe : Hg alloys. — The photoelectric cross section of nuclear detector materials varies as $Z^{4.5}$ in the range from 1 keV to 1 MeV. Following an idea of C. Hilsum (R. S. R. E.) we have undertaken the preparation of cadmium rich CdTe/HgTe alloys to increase the average atomic number of CdTe. The composition $\text{Cd}_{0.9}\text{Hg}_{0.1}\text{Te}$ theoretically corresponds to an increase of 15 % of the photoelectric cross-section.

Experimental. — Little has been reported on the preparation of CdTe : HgTe solid solutions with a high concentration of cadmium telluride. Their high melting points lead to very large mercury vapour pressures which render the preparation difficult. We have used the THM process using Te as the solvent. The source material was a cylinder of diameter 15 mm. It consisted of two cylindrical sectors — one in CdTe and the other one in HgTe — whose cross-sections were in a ratio corresponding to the desired composition.

The cadmium telluride ingot was obtained by the sealed ingot zone refining technique, and the mercury telluride ingot from simultaneous synthesis and growth by THM with tellurium solvent, the source material being constituted by a stoichiometric mixture of liquid mercury and tellurium powder [23].

For the composition $\text{Cd}_{0.9}\text{Hg}_{0.1}\text{Te}$, whose melting point (liquidus point) is of around 1 062 °C [24], the main parameters were adjusted to the following values : growth temperature 700 °C, growth rate : 3 mm per day.

Results. — Ingots of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ were grown mainly in the range $x \sim 0.9$, without doping and with chlorine as doping agent. Picture 7 illustrates the crystallinity of three sections cut from the head, middle and bottom of an ingot. The growth direction does not correspond to any simple crystallographic axis.

The homogeneity has been measured using an electronic microprobe. No composition variation has been found on the sections, that is in a direction normal to

FIG. 7. — Sectional views of a THM $\text{Cd}_{0.9}\text{Hg}_{0.1}\text{Te}$: ingot (a) top, (b) middle (c), bottom.

the growth axis. The longitudinal profile of an ingot is pictured on figure 8. The greatest part of the ingot presents a very satisfactory homogeneity. Some foreseeable composition variations are found near the head and the bottom of the ingot. The room temperature energy gap has been measured by optical transmission for the composition $x \sim 0.9$ and for compositions ranging between 0.9 and 1. The results, presented figure 8, show an almost linear variation in this composition range.

FIG. 8. — Dependence of the room temperature energy gap versus composition of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys.

The following room temperature electrical characteristics have been measured on an undoped crystal, with $x \sim 0.9$: $p = 4.7 \times 10^{15} \text{ cm}^{-3}$, $\rho = 29 \Omega \times \text{cm}$, $\mu = 45 \text{ cm}^2/\text{V.s}$. We have not been able to change the type of such a crystal by annealing under cadmium vapour.

We have tried to obtain semi-insulating crystals, with $x \sim 0.9$, suitable for γ nuclear detection, by compensating during the THM process with chlorine introduced in the form of CdCl_2 in the tellurium charge.

FIG. 9. — Dependence of the composition versus the position along the ingot growth axis for a $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ ingot with $x \sim 0.9$.

The ingot was n-type in its first part, with the following room temperature electrical characteristics :

$$n = 9.2 \times 10^{12} \text{ cm}^{-3}, \quad \rho = 1\,100 \, \Omega \times \text{cm}, \\ \mu = 600 \text{ cm}^2/\text{V.s},$$

and became semi-insulating in the last third part.

4. Conclusion. — Some aspects of the thermodynamic state of CdTe crystals obtained by different zone passing techniques are considered, and the requirements to obtain high resistivity crystals are discussed. Very pure crystals have been prepared by a new vapour growth technique called *sublimation THM*, as confirmed by electrical and photoluminescence measurements : room temperature hole mobilities as high as $100 \text{ cm}^2/\text{V.s}$ were found while, in photoluminescence, only a sharp excitonic line dominates the spectra registered at low temperature. This sublimation THM decreases the concentration of tellurium precipitates, with regard to classical THM, while keeping most of its advantages. Large and homogeneous $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ crystals, mainly with $x \sim 0.9$, have been grown by THM using Te solvent. Semi-insulating crystals can be obtained when chlorine is introduced during the THM process.

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